



Crater functions for compound materials: A route to parameter estimation in coupled-PDE models of ion bombardment

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Molecular Dynamics estimation of coefficients for irradiated binary alloys: Testing the Bradley-Shipman theory

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Abstract

Coupled PDE models describing both morphological and chemical evolution, such as recently introduced by Bradley and Shipman, offer a promising potential explanation for the highly-ordered patterns sometimes observed during the irradiation of binary compounds with low-energy ions. However, as currently employed in several contexts, these models require specific conditions on a number of unknown parameters to explain this behavior. Specifically, they require that the effect on surface morphology of atoms sputtered away from the surface is larger than the effect of the atoms merely redistributed to new locations on the surface, a formerly-common assumption that has recently been overturned for several pure materials. Here, we develop a framework in which many of the parameters of the BS theory can be estimated using the results of molecular dynamics simulations. By adapting the recent theory of “crater functions” to the case of binary materials, we are able to establish relationships between the parameters in coupled PDE models and various moments of the statistically-averaged crater function associated with single ion impacts. Applying our framework to the commonly-studied GaSb system, we find that the requirement of erosive dominance is not fulfilled, motivating the consideration of other potential pattern-forming mechanisms.

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I. INTRODUCTION

The irradiation of flat surfaces by low-energy ions can lead to the emergence of ordered arrays of nanoscale surface features [1], and offers a potential to assist in the fabrication of nanostructured devices with regular structure [2]. Initially observed on a wide variety of target materials [3–5], careful experimental investigation has led to a growing consensus that these structures only appear during the irradiation of binary materials, or environments in which one or more materials is simultaneously co-deposited during the irradiation process [6–11]. This consensus has motivated a number of theoretical treatments of irradiated binary materials, tracking the evolution of both the morphology and the concentration. Extending the pioneering work of Shenoy, Chan, and Chason [12], Bradley and Shipman (BS) have recently introduced such a theory exhibiting the first physically-grounded explanation for the strong ordering of the observed nanostructures [13, 14]. This result has sparked great interest, inspiring additional studies on normal-incidence irradiation of two-component materials [15], including a variant where the second material is not originally present, but instead co-deposited simultaneously with the ion irradiation [16], and a similar framework for the study of ion-assisted deposition, where both materials are deposited along with the ions, and the deposition rate exceeds the sputtering rate [17].

Despite its success, however, the family of models initiated by Bradley and Shipman face some important open questions. At a general level, they contains many parameters whose values are so far undetermined. Because the BS theory only admits ordered structures for specific regions of parameter space, it is important to identify whether common experimental systems have parameters within those regions. So far, such estimation does not appear to have been performed. More specifically, it assumes that the fundamental driving force behind the instability is the erosive mechanism identified by Bradley and Harper [18], implying that the surface should be unstable even in the absence of a second species. This has formerly been a common assumption in the field, but has recently been overturned for the case of the pure materials Silicon and Germanium [19, 20], where flat surfaces are observed at normal incidence, attributed to the dominance of redistributed atoms over sputtered atoms [21–23] (though beam-induced stress within a thin layer of

amorphized material also serves to stabilize surfaces at normal incidence [24–26]). The important question we will pursue, then, is to determine whether this dominance extends to the case of binary materials, and if so, to identify the consequences for existing theories.

We will begin in Section II with a necessary, brief review of the key features of the Bradley-Shipman theory: its equations, parameters, the ordered patterns it predicts, and especially the parameter regime necessary to obtain those patterns. Then, in Section III, we begin our main task: the development of a framework for the estimation of several of the parameters, by means of an extension of the theory of crater functions [23, 27] to the case of binary materials. We demonstrate how this generalization leads, as in the case of pure materials, to a continuum equation for the evolution of the surface height in terms of moments of the crater functions. Comparing that equation to those of Bradley and Shipman, we then obtain relationships between parameters in the latter theory to the crater function moments in the former, which can be estimated using molecular dynamics simulation. Finally, in Section IV, we perform such simulations of irradiated Gallium Antimonide (GaSb) - the experimental system in which ordered dots were first observed [1], and which remains of experimental interest within the ion-beam patterning community [28, 29]. Using the the framework developed in Section III, we estimate parameters for this system, finding that redistributed atoms continue to dominate over sputtered atoms for GaSb under low-energy argon irradiation, and concluding that the BS model may not actually be able to explain the finite wavelength bifurcation in this system. A discussion of the implications follows in Section V.

II. REVIEW OF THE BRADLEY-SHIPMAN THEORY: MODEL AND STABILITY ANALYSIS

We begin by briefly summarizing the recent model of Bradley and Shipman [13, 14] for irradiated binary materials, which itself builds upon the earlier model of Shenoy et al. [12]. Because extensive analysis of this class of models exists elsewhere, both in general [30], and in the context of ion irradiation [12–14, 17], we will be as brief as possible. However, because our aim is to test specific aspects of this theory and others like it, we must include those results that are directly relevant to the molecular dynamics simulations we perform at the end. (Note: when referring to specific equations within the BS theory, we

refer to the longer and more detailed Ref. [14], despite the earlier publication of Ref. [13]).

A. Model

The Bradley-Shipman model tracks the evolution of a height field $z = h(x, y, t)$ describing the irradiated surface, and concentration fields $c_A(x, y, t)$ and $c_B(x, y, t)$ of two components A and B . Under the effects of preferential erosion, a steady state is reached in which the material is receding with constant velocity v_0 and constant surface concentrations $c_{A,0}$ and $c_{B,0}$ of A and B atoms, respectively. The stability of this steady state is investigated by introducing perturbations to this steady state via the equations

$$\begin{aligned} h &= -v_0 t + u(x, y, t) \\ c_A &= c_{A,0} + \phi(x, y, t) \\ c_B &= c_{B,0} + (1 - \phi(x, y, t)) \end{aligned}$$

where $u(x, y, t)$ describes the perturbation to the height field, and $\phi(x, y, t)$ describes the perturbation to the concentration field of species A . After some significant modeling and analysis (Eqs. (3)-(13) of Ref.[14]) the following linearized equations for the evolution of u and ϕ are obtained:

$$\frac{\partial u}{\partial t} = -A\phi + C\nabla^2 u - D\nabla^4 u \quad (1)$$

$$\frac{\partial \phi}{\partial t} = -A'\phi + B'\nabla^2 \phi + C'\nabla^2 u, \quad (2)$$

where we have continued to employ the reasoning in Ref.[14] used to neglect terms $B\nabla^2 c$ in Eqn.(1) and $\delta\nabla^4 h$ in Eqn.(2). In a slight deviation from Ref.[14], we will assume that species A is preferentially sputtered (rather than species B), and define coefficients in such a way that zeroth- and fourth-order terms in Eqs.(1)-(2) have negative sign, whereas second-order terms have positive sign. The coefficients in Eqn.(1) for the height evolution are defined via

$$\begin{aligned}
A &= P_0 \Omega [\Lambda'_A (c_{A,0}) - \Lambda'_B (c_{B,0})] > 0 \\
C &= \Omega [(\mu_A (c_{A,0}) + \mu_B (c_{B,0})) - \alpha (\Lambda_A (c_{A,0}) + \Lambda_B (c_{B,0}))] \\
D &= [c_{A,0} D_A + c_{B,0} D_B] \frac{n_s \Omega^2 \gamma_s}{k_B T} > 0
\end{aligned} \tag{3}$$

and in Eqn.(2) for the concentration evolution, via

$$\begin{aligned}
A' &= \frac{P_0 \Omega}{\Delta} [c_{B,b} \Lambda'_A (c_{A,0}) + c_{A,b} \Lambda'_B (c_{B,0})] > 0 \\
B' &= \frac{n_s \Omega}{\Delta} [c_{B,b} D_A + c_{A,b} D_B] > 0 \\
C' &= \frac{\Omega}{\Delta} [c_{B,b} \mu_A (c_{A,0}) - c_{A,b} \mu_B (c_{B,0})]
\end{aligned} \tag{4}$$

Here P_0 is the power deposited by the ions per unit surface area on a flat surface, Ω is the atomic volume (taken to be the same for both species), n_s is the total number of mobile surface atoms per unit area on the surface, γ_s is the surface energy, k_B is Boltzmann's constant, T is the temperature, Δ is the amorphous film thickness, $c_{A,0}$ and $c_{B,0}$ are the concentration of A and B atoms in the film at steady state, $c_{A,b}$ and $c_{B,b}$ are the concentration of A and B atoms in the bulk, D_A and D_B are the diffusivities of A and B atoms, $\Lambda_A (c_A)$ and $\Lambda_B (c_B)$ are proportionality constants linking the deposited power to the sputtering rate, and $\mu_A (c_A)$ and $\mu_B (c_B)$ are proportionality constants describing preferential redistribution of material, an effect first proposed in Refs.[13, 14] and playing a critical role therein.

B. Generic Stability Analysis

To determine the presence or absence of an instability, it is sufficient to consider a one-dimensional perturbation, because of the isotropic nature of normal-incidence irradiation. Without loss of generality, we may orient this instability in the x -coordinate direction, giving

$$\begin{bmatrix} u(x, t) \\ \phi(x, t) \end{bmatrix} = \begin{bmatrix} u_1 \\ \phi_1 \end{bmatrix} e^{ikx + \sigma t}, \tag{5}$$

where k is the wavenumber of the perturbation, σ the growth rate of that perturbation, and u_1 and ϕ_1 are undetermined constants describing the relative phases and magnitudes of the

height and concentration modulations. Inserting the perturbation (5) into the governing equations (1)-(2), we obtain, in matrix form,

$$\begin{bmatrix} \sigma + Ck^2 + Dk^4 & A \\ C'k^2 & \sigma + A' + B'k^2 \end{bmatrix} \begin{bmatrix} u_1 \\ \phi_1 \end{bmatrix} = \mathbf{0}. \quad (6)$$

For a solution $[u_1, \phi_1]^T$ of this equation, the determinant of the matrix must be zero, giving a the dispersion relation $\sigma(k)$ in the quadratic form

$$\sigma^2 + \tau\sigma + \Delta = 0, \quad (7)$$

where $\tau(k)$ and $\Delta(k)$ are respectively the trace and determinant of (6) when $\sigma = 0$:

$$\tau(k) = A' + (C + B')k^2 + Dk^4 \quad (8)$$

$$\Delta(k) = (CA' - AC')k^2 + (CB' + DA')k^4 + (DB')k^6. \quad (9)$$

For the purpose of identifying stability properties, it is sufficient to consider only the root associated with the '+' sign in the quadratic formula which, following common practice, is denoted $\sigma_+(k)$:

$$\sigma_+(k) = \frac{1}{2} \left(-\tau + \sqrt{\tau^2 - 4\Delta} \right). \quad (10)$$

This gives the growth rate of the faster-growing solution when the discriminant is positive.

C. Discussion: Requirements for Ordered Patterns

The expected behavior of an initially-flat surface is determined by nature of the function $\sigma_+(k)$, extensively discussed in Refs. [30, 31]. Wavenumbers k for which $\sigma_+(k) < 0$ are stable and decay over time, while those k for which $\sigma_+(k) > 0$ are unstable and grow over time. The essential first ingredient for producing ordered patterns is the presence of a narrow band of unstable wavenumbers surrounded on both sides by stable regions. In particular, the very-smallest wavenumbers corresponding to very long wavelengths must be stable; otherwise the system will tend to exhibit disordered kinetic roughening phenomena. An important accomplishment of the Bradley-Shipman theory was its identification of such a narrow band in the Equations(1)-(2). Although Eqs.(1)-(2) contain six parameters, the conditions under which such an instability can occur are quite limited. This is most easily seen via a brief qualitative simplification of the analysis in Ref.[14].

First, we consider the conditions under which an instability of any kind may exist. Examining Equation (10), we see that the system is stable if both $\tau > 0$ and $\sigma > 0$, but unstable if either one is negative. From the definitions (8)-(9), we see that because the parameters A , D , A' , and B' are all positive, this can only occur if one of either C or $(A'C - C'A)$ is negative. Second, turning to the requirement, for ordered patterns, that long wavelengths be stable (to form a narrow band), we examine Eqs. (8)-(10) in the limit as $k \rightarrow 0$, and find that for small values of k

$$\lim_{k \rightarrow 0} \sigma_+(k) \approx -\frac{1}{A'} (A'C - C'A) k^2 + \mathcal{O}(k^4). \quad (11)$$

To stabilize the longest-wavelength modes, we must therefore impose the requirement

$$A'C > C'A. \quad (12)$$

From the above considerations, we immediately conclude that an instability with a narrow band of unstable wavenumbers is only possible if (a) C is sufficiently negative to drive the instability, and (b) γ is sufficiently negative to stabilize the long waves. These are striking requirements of the Bradley-Shipman instability. The first implies the existence of an morphologically-driven instability [18] even in the absence of concentration modulations ($c_1 \equiv 0$). While formerly a common assumption, this has recently been overturned for pure Silicon and Germanium [19, 20], where there is strong evidence that in fact $C > 0$ due to the dominance of redistributive over erosive effects [23]. Although binary systems are *chemically* different from pure silicon, the collision cascade leading to both erosion and redistribution is a predominantly *kinetic* process (although chemical effects have been identified in collision cascades, they do not affect atom redistribution strongly [32, 33]). Hence, the dominance of redistribution over erosion might be expected to persist in binary system. The second requirement of the BS instability, of strongly negative C' , is also somewhat surprising, for it implies that the preferentially-sputtered material is much less likely to be displaced within the collision cascade. These features highlight the importance of being able estimate parameters within the BS theory, and we now illustrate how this may be done via molecular dynamics.

III. COEFFICIENT ESTIMATION VIA MOLECULAR DYNAMICS

A. Crater Functions for compound targets

To estimate parameters in two-component models such as the BS theory, we must first develop a framework within which the results of MD simulation may be connected to the coefficients of Eqs.(1)-(2). To this end, we will generalize the “crater function” theory for surface morphology evolution [23, 27] to the case of a multi-component material, obtaining continuum equations of a form similar to Eqn.(1). Essentially, we need only revise the definition of the “crater function” $\Delta h(x, y; \theta)$, describing the average change in surface morphology to a flat surface due to the impact of a single ion at the origin, so that it is composed of four parts:

$$\Delta h(x, y; \theta, c_A, c_B) = \Delta h_A^{\text{eros.}} + \Delta h_B^{\text{eros.}} + \Delta h_A^{\text{redist.}} + \Delta h_B^{\text{redist.}} \quad (13)$$

This merely states that the change in surface topography due to a single ion impact is the superposition of effects due to both eroded and redistributed atoms, of both Ga and Sb. A central benefit of this approach is that any subsequent analytical treatment of Δh treats all these effects identically, and so long as all operations on Δh are linear, the final contribution to continuum equations can be broken out into component parts at the end of the analysis. Hence, because the analysis of Ref.[27] (and a simplified approximation for flat targets in Ref.[23]) has already been performed for a general Δh , all the results therein continue to be valid for the present case.

Using Eqs.(46) and (48) in Ref.[27] as a template, we define

$$\begin{aligned} \Delta h_A^{\text{eros.}} &= -\Omega_A \sum_i \delta(\mathbf{x}_i^I) \\ \Delta h_B^{\text{eros.}} &= -\Omega_B \sum_j \delta(\mathbf{x}_j^I) \\ \Delta h_A^{\text{redist.}} &= \Omega_A \sum_k \delta(\mathbf{x}_k^F) - \delta(\mathbf{x}_k^I) \\ \Delta h_B^{\text{redist.}} &= \Omega_B \sum_l \delta(\mathbf{x}_l^F) - \delta(\mathbf{x}_l^I) \end{aligned}$$

where the Ω denote atomic volumes, i, j denote sputtered A, B atoms, k, l denote displaced A, B atoms, and \mathbf{x}^I and \mathbf{x}^F denote initial and final target atom positions associated with

an ion impact. When the crater function is integrated to obtain moments, these four components produce associated contributions to the zeroth and first moments. Following Eqs.(47) and (49) of Ref.[27], we obtain:

$$\begin{aligned}
M_A^{(0)} &= \int \Delta h_A^{\text{eros.}} dA &= -\Omega_A \sum_i 1 \\
M_B^{(0)} &= \int \Delta h_B^{\text{eros.}} dA &= -\Omega_B \sum_j 1 \\
M_{A,\text{eros.}}^{(1)} &= \int \mathbf{x} \Delta h_A^{\text{eros.}} dA &= -\Omega_A \sum_i \mathbf{x}_i^{\text{I}} \\
M_{B,\text{eros.}}^{(1)} &= \int \mathbf{x} \Delta h_B^{\text{eros.}} dA &= -\Omega_B \sum_j \mathbf{x}_j^{\text{I}} \\
M_{A,\text{redist.}}^{(1)} &= \int \mathbf{x} \Delta h_A^{\text{redist.}} dA &= \Omega_A \sum (\mathbf{x}_k^{\text{F}} - \mathbf{x}_k^{\text{I}}) \\
M_{B,\text{redist.}}^{(1)} &= \int \mathbf{x} \Delta h_B^{\text{redist.}} dA &= \Omega_B \sum (\mathbf{x}_l^{\text{F}} - \mathbf{x}_l^{\text{I}})
\end{aligned} \tag{14}$$

Finally, following a multi-scale analysis, these contributions to the moments produce associated terms in the governing equation for the height field

$$\begin{aligned}
h_t &\approx (Y^A + Y^B) \\
&+ \left(S_X^{A,\text{eros.}} + S_X^{B,\text{eros.}} + S_X^{A,\text{redist.}} + S_X^{B,\text{redist.}} \right) h_{xx} \\
&+ \left(S_Y^{A,\text{eros.}} + S_Y^{B,\text{eros.}} + S_Y^{A,\text{redist.}} + S_Y^{B,\text{redist.}} \right) h_{yy}
\end{aligned} \tag{15}$$

with definitions given by Eqn.(4) of Ref.[23]

$$\begin{aligned}
Y^Z(\theta, c_i) &= \left[I_0 \cos(\theta) M_Z^{(0)}(\theta, c_i) \right] \\
S_X^{Z,\text{type}}(\theta, c_i) &= \frac{\partial}{\partial \theta} \left[I_0 \cos(\theta) M_{Z,\text{type}}^{(1)}(\theta, c_i) \right] \\
S_Y^{Z,\text{type}}(\theta, c_i) &= \left[I_0 \cos(\theta) \cot(\theta) M_{Z,\text{type}}^{(1)}(\theta, c_i) \right]
\end{aligned} \tag{16}$$

where Z is either A or B and 'type' is either 'eros.' or 'redist.' (see Section IV C for further comments on these formulas). In addition, I_0 is the flux through a plane perpendicular to the beam, which is not defined within the simulation of a single impact.

B. Relationship to BS Theory

Upon comparison with BS theory, it is easily seen that the coefficients of the terms h_{xx} and h_{yy} (which are equal at normal incidence due to rotational symmetry) correspond

exactly with the coefficient C in Eqn.(1). However, the various quantities Y and S in Eq.15 allow estimation of the physical parameters underlying C , which critically also appear in other parameters. We will see that the results of molecular dynamics in the form of the coefficients 16 provide enough information to estimate fully four coefficients $\{A, C, \alpha, \gamma\}$ from the Bradley-Shipman theory.

Before we proceed, we make one important simplifying assumption. The various components of the moments $M^{(0)}$ and $M^{(1)}$ are functions not only of angle, but also of the concentrations of the various species within the target. Similarly, within the BS theory, the quantity Λ_i - associated with sputter yield - and presumably also μ_i - describing the redistributive flux - share this dependence. [The latter dependence was not discussed in Ref.[14], but presumably exists.] As an alternative to performing simulations at many different concentrations, we will here make the assumption on the moments that

$$\begin{aligned} M_{\text{sp.}}^{(0)}(c_{\text{sp.}}) &= M^{(0)}\left(\frac{1}{2}\right) \times (2c_i) \\ M_{\text{sp.}}^{(1)}(c_{\text{sp.}}) &= M^{(1)}\left(\frac{1}{2}\right) \times (2c_i) \end{aligned} \tag{17}$$

and the corresponding assumption, within the BS theory, that

$$\begin{aligned} \Lambda_i(c_i) &= \Lambda_i\left(\frac{1}{2}\right) \times 2c_i \\ \mu_i(c_i) &= \mu_i\left(\frac{1}{2}\right) \times 2c_i \end{aligned} \tag{18}$$

That is, each species both sputters and redistributes at a rate *linearly* proportional to its concentration in the film, with rate zero when its concentration is zero, and rate equal to our measured rate when its concentration is one half. This will allow estimation of derivatives with respect to concentration in the vicinity of the naturally-occurring 50/50 concentration, without excessive numerical simulation (see Section IV C below for further discussion).

With the approximations given by Eqs.(17)-(18), we are now able to obtain a direct relationship with the theory of Bradley and Shipman by directly comparing Eqn.(15) with Eq.(7) in Ref.[14]. Although these equations were obtained by different means, they describe precisely the same phenomenon, based on an identical set of physical mechanisms. We therefore equate them in a term-by-term manner for the case of normal incidence

($\theta = 0$). Using also Eqs.(3-6) of Ref.[14], we see that the various coefficients (16) extracted from the crater function moments must be equal to parameter combinations in Ref.[14] as follows:

$$\begin{aligned}
\Omega_A P_0 \Lambda_{A,0} &= -2Y^A(0, 0.5) \times c_{A,0} \\
\Omega_B P_0 \Lambda_{B,0} &= -2Y^B(0, 0.5) \times c_{B,0} \\
\Omega_A \alpha \Lambda_{A,0} &= -2S_{X,Y}^{A,\text{eros.}}(0, 0.5) \times c_{A,0} \\
\Omega_B \alpha \Lambda_{B,0} &= -2S_{X,Y}^{B,\text{eros.}}(0, 0.5) \times c_{B,0} \\
\Omega_A \mu_{A,0} &= 2S_{X,Y}^{A,\text{redist.}}(0, 0.5) \times c_{A,0} \\
\Omega_B \mu_{B,0} &= 2S_{X,Y}^{B,\text{redist.}}(0, 0.5) \times c_{B,0}
\end{aligned} \tag{19}$$

where the Y and S terms are estimated for $\theta = 0$ and at the 50/50 concentration, and the estimation of the values at the steady concentration are attained by means of Eqs.(17)-(18). Finally, combining the relationships (19) with the definitions for $\{A, C, A', C'\}$ in Eqs.(3)-(4), we can then estimate these parameters as follows

$$\begin{aligned}
A &= -2(Y^A - Y^B) > 0 \\
C &= 2 \left(c_{A,0} S_{X,Y}^{A,\text{eros.}} + c_{B,0} S_{X,Y}^{B,\text{eros.}} + c_{A,0} S_{X,Y}^{A,\text{redist.}} + c_{B,0} S_{X,Y}^{B,\text{redist.}} \right) \\
A' &= -\frac{2}{\Delta} (c_{A,b} Y_B + c_{B,b} Y_A) > 0 \\
C' &= \frac{2}{\Delta} \left(c_{B,b} c_{A,0} S_{X,Y}^{A,\text{redist.}} - c_{A,b} c_{B,0} S_{X,Y}^{B,\text{redist.}} \right)
\end{aligned} \tag{20}$$

We see that fully four out of six of the BS parameters are accessible to MD studies. These are notable for a number of reasons. Of significant general interest, these happen to be precisely the parameters that govern the behavior of the longest wave perturbations to the surface height, via the finite-wavelength requirement in Eq.(12). Thus, the results of MD simulation may be used to predict whether an irradiated binary system has long-wave or finite-wavelength instabilities. Of more specific interest here, these parameters include both C and C' , and so may be used to test specific requirements of the BS theory.

IV. MOLECULAR-DYNAMICS ESTIMATION OF COEFFICIENTS

A. Simulation Environment

Using molecular dynamics simulations, we have estimated the quantities in Eq.(16) for the case GaSb irradiated by Ar ions at 250 eV. Amorphous GaSb was created by annealing a cubic piece of initially crystalline GaSb, consisting of 1.1×10^4 atoms. In these simulations periodic boundary conditions were used. Copies of the obtained amorphous GaSb were joined together (3 in the x - and y -directions, and 2 in the z -direction) to form a target consisting of nearly 2.0×10^5 atoms. The surface of the target was finally relaxed at 0 K, with periodicity only in the x - and y -directions. In the bombardment simulations periodic boundary conditions were used in the x - and y -directions. The simulation time was 250 ps, which is rather long, but turned out to be necessary for the post-impact atomic movements to seize.

The inter-atomic potentials used for Ga-Sb interactions was that of Powell et al [34]. The (rarely occurring) pure Ga interactions were the same as those in the GaAs potential developed by us [35]. To obtain the Sb potential, we note that As and Sb have the same crystal structure. Hence, the As potential parameter D_e [35] was rescaled with the difference in cohesive energies of the two elements, and the parameter r_0 with the difference in lattice constants. This gave a cohesive energy of 2.72 eV/atom and a density of 7.28 g/cm^3 for pure Sb, in reasonable agreement with the experimental values of 2.72 eV/atom and 6.74 g/cm^3 . We emphasize that since regions of pure Ga or Sb should not form in the simulated system, the results are not expected to be sensitive to small inaccuracies in the description of the pure elements.

At each of nine different irradiation angles, we simulated 300 independent Ar ion impacts onto the target just constructed. Each ion hit the target at a random location, and for off normal incidence, arrived from a random azimuthal angle. As discussed in Ref.[23], two sources of noise were first filtered from the data before the moments were measured. First, despite the careful preparation of the target, some residual stresses remain, leading to displacements during the simulation that are due to the pre-existing state of the target, rather than to the impact. Second, the periodic nature of the cell allows small coherent shears to occur, on the scale of the entire cell. These are both filtered by constructing an

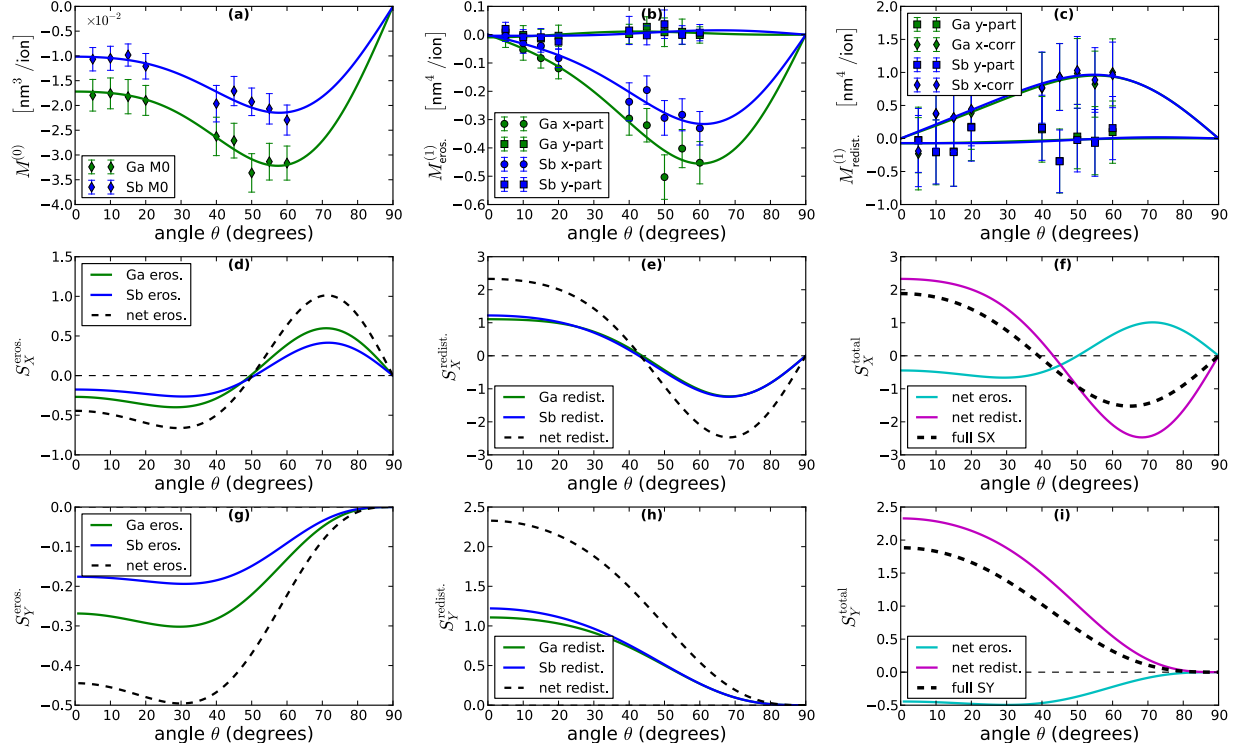


Figure 1. Moments and coefficients by component. (a) The decomposition of the zeroth moment $M^{(0)}$, indicates that Ga is preferentially sputtered from a homogeneous amorphous film at 50/50 initial concentrations. (b) The decomposition of the first erosive moment $M_{\text{eros}}^{(1)}$, indicates that Ga endures a stronger curvature-dependent sputtering. (c) The decomposition of the first redistributive moment $M_{\text{redist}}^{(1)}$, indicates the preferential redistribution is not a dominant effect. (d) The erosive component of S_X for both species. (e) The redistributive component of S_X for both species. (f) A comparison of net erosive and redistributive contributions to the net coefficient S_X . (g)-(i) The corresponding plots for S_Y (for completeness). As has been seen for pure silicon, the stabilizing redistributive contribution overwhelms the destabilizing erosive contribution at low angles.

annulus around the impact cite, and calculating both the average lab-frame displacement of each atom, as well as the average shear in a co-ordinate system aligned with the incoming ion direction. Both averages were then subtracted from the displacement field, after which moments were calculated according to Eq.(14).

B. Results

The results of our simulations are shown in Fig.1. We first calculate the moments according to Eq.(14), and plot them along with three-term Fourier fits with expected symmetries imposed (see Ref.[23]). Our Fig.1a indicates that, for an initial fresh, unsegregated 50/50 target, Ga is preferentially sputtered relative to Sb (see Section IV C below for a discussion of this result); therefore we set $A = \text{Ga}$ and $B = \text{Sb}$ in the framework of Section III. A comparison of Figure 1b and 1c supports our hypothesis that redistributive components of the first moment are of larger magnitude than the erosive components. In addition, the redistributive moments appear strikingly similar between species, indicating that preferential redistribution is unlikely to be a significant effect for this system. To confirm that these impressions are not altered under the derivatives in Eqs.(16), we also plot the coefficients found in that equation in Figures 1d-i. We see, as in the case of pure silicon, an expected positive value for the net values of S_X and S_Y at normal incidence, when summed over all species and effects. Furthermore, we are able to provide the first prediction of the effect of preferential redistribution, and have found it unlikely to be important.

Using the data shown in Figure 1, and the definitions of the coefficients from Eqs.(16), we obtain the values

$$\begin{aligned}
 Y^{\text{Ga}}|_{\theta=0} &= -0.0172 \times I_0 \frac{\text{nm}}{\text{s}} \\
 Y^{\text{Sb}}|_{\theta=0} &= -0.0102 \times I_0 \frac{\text{nm}}{\text{s}} \\
 S_{X,Y}^{\text{Ga,eros.}}|_{\theta=0} &= -0.269 \times I_0 \frac{\text{nm}^2}{\text{s}} \\
 S_{X,Y}^{\text{Sb,eros.}}|_{\theta=0} &= -0.176 \times I_0 \frac{\text{nm}^2}{\text{s}} \\
 S_{X,Y}^{\text{Ga,redist.}}|_{\theta=0} &= 1.11 \times I_0 \frac{\text{nm}^2}{\text{s}} \\
 S_{X,Y}^{\text{Sb,redist.}}|_{\theta=0} &= 1.22 \times I_0 \frac{\text{nm}^2}{\text{s}}
 \end{aligned} \tag{21}$$

where I_0 is again the flux in the beam direction, as in Eq.(16). From Eq. (12) of Ref.[14], together with the relationships in Eq.19 for Y^{Ga} and Y^{Sb} , we can obtain the predicted

steady concentrations of Ga and Sb to be

$$c_{\text{Ga},0} = 0.37$$

$$c_{\text{Sb},0} = 0.63$$

Then, following the relationships (20), we convert these values into estimates for $\{A, C, A', C'\}$ of

$$\begin{aligned} A &\approx 0.014 \times I_0 \frac{\text{nm}}{\text{s}} \\ C &\approx 1.94 \times I_0 \frac{\text{nm}^2}{\text{s}} \\ A' &\approx .0091 \times I_0 \frac{1}{\text{s}} \\ C' &\approx -.12 \times I_0 \frac{\text{nm}}{\text{s}} \end{aligned}$$

where we have taken the value $\Delta \approx 3 \text{ nm}$ from the irradiation of pure silicon at 250 eV [36]. These estimations exhibit three salient features: (1) the parameter C is positive, consistent with findings for pure materials, and contrary to the assumptions of BS theory; (2) the parameter group $C'A$ in Eq.(9) (the only place that C' occurs) is much smaller than the similarly-dimensioned group $A'C$, indicating that preferential redistribution is likely not an important effect; and (3) the parameter group $(A'C - C'A)$ is positive, indicating that long wave perturbations are stabilized. The first two findings are contrary to the assumptions of BS theory. Together with the third, and according to the discussion in Section II C, they imply that, in fact, that theory should predict stable, flat surfaces for irradiation of GaSb.

C. Limitations.

We want to acknowledge the following limitations in our approach.

First, the definitions for the coefficients Y^Z and $S^{Z,\text{type}}$ in Eq.(16), like the corresponding definitions in Ref.[23] from which they are generalized, are the result of performing simulated impacts on an initially flat target surface. As such, they represent simplifications of the more general results in Ref.[27] for curved surfaces. Obtaining the latter would, unfortunately, require simulation of impacts not only over many angles, but also on many

different types of curved surface, which is outside our current computational capacity. It is our belief that this simplification does not significantly change the relative strength of erosion vs. redistribution.

Second, our simulations were performed only at the 50/50 concentration for a fresh, homogeneous target, and values of coefficients at the steady concentration were inferred by means of the linear approximations in Eqs. (17)-(18). Like the flat-surface simplification, this avoids the simulation of targets at a variety of concentrations. Were more accurate estimates desired, such simulations could of course be performed. However, in addition to the computational cost of the simulations themselves, this would require the construction of many targets, which is in fact the most time-consuming part of our study. In addition, the nature of the irradiated target away from the 50/50 concentration is not currently well-known.

Third, our results indicate that Ga is sputtered preferentially relative to Sb for a fresh, unsegregated target at the 50/50 concentration. This would imply the rapid enrichment of Sb near the surface, in direct contrast to experimental observations of excess Ga at the surface of this material. (more recent in situ observations made in an environment devoid of oxygen show that, while not as strong in the absence of oxygen, Ga enrichment is still observed [29].) Because of the disparate experimental results, our MD result was checked against the results of SRIM, which predicted much more similar yields of the two species, but still with a 2% enhanced yield for Ga over Sb. Both the MD and the BCA thus give a result consistent with the more-efficient transfer of energy in Ar/Ga collisions relative to that in Ar/Sb collisions. It may thus be that actual experimental conditions differ from the ones we have simulated in ways that still need to be understood.

Bringing the simulated results into agreement with experiment will require a better understanding of precisely what is happening during the early stages of irradiation, and the construction of an atomistic target reflecting that understanding. Nevertheless, anticipate that our principal conclusions are likely to remain valid for a more accurate set of targets. For instance, we found the redistributive component of the coefficient C - of central importance to the Bradley-Shipman theory - to be around five times greater than the erosive component. Because C represents the effects of *net* erosion and redistribution, it therefore should not be especially sensitive to the exact composition of the target, and

this dominance should be expected to continue. Similarly, although the groups AC' and CA' contain the effects of preferential displacements, and may be expected to vary more with concentration, we find that CA' is more than ten times greater than AC' - a difficult ratio to reverse under any circumstances.

V. CONCLUSIONS

Subject to the limitations just described, we have shown that four parameters of the Bradley-Shipman theory and other similar theories are accessible to Molecular Dynamics simulation by means of an extension, to binary materials, of the theory of crater functions described in [23, 27]. These parameters are A , C , A' , and C' , describing net sputtering and redistribution (C), preferential sputtering (A), preferential redistribution (C'), and material replenishment (A'). Remarkably, these are exactly the four parameters needed to calculate the critical parameter group $(A'C - C'A)$, which governs the behavior of long waves. The methods demonstrated here are general, and should therefore be applicable to a wide variety of coupled PDE models for irradiated binary systems [13, 14], enabling the prediction of this important distinguishing characteristic among a variety of pattern-forming systems.

Subsequently, we have performed the first estimate of these four parameters for the specific system of low-energy irradiation of GaSb by Ar, in which hexagonal dot arrays were first observed. Our main finding for this system is that the parameter C , associated with net erosion vs. net redistribution, is positive, indicating the dominance of redistribution over erosion, as was predicted by MD for pure Si [23], and shown experimentally for both pure Si and Ge [19, 20]. Additionally, we saw that the parameter γ associated with preferential redistribution, hypothesized to be an important physical effect in ordered dot formation, is too small to play an important role, at least for this particular system. An interesting topic for future study will be to determine whether this tends to be true in general.

Both the positive value of C , and the relative unimportance of C' , are contrary to the finite-wavelength requirements of the Bradley-Shipman theory. In fact, for the parameter values we have estimated, that theory would predict entirely smooth surfaces for low-energy, normal-incidence irradiation of GaSb. Especially if the dominance of the redistribu-

tive component of the collision cascade extends to a wide range of other two-component materials (in other words, if it is a generic property of the kinetically-dominated collision cascade), then this finding provides strong motivation for the consideration of alternative physical mechanisms to explain the ordered patterns observed in these systems. We investigate such a mechanism elsewhere [37].

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